Vapor-Liquid Equilibria in the Acetone–2,3-Dimethylbutane and Chloroform–2,3-Dimethylbutane Systems

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Vapor-liquid equilibrium data were determined on the acetone–2,3-dimethylbutane and the chloroform–2,3-dimethylbutane systems at 760 mm. of mercury pressure. A minimum boiling azeotrope was estimated to occur at $x_{acetone} = 0.47$ and at 44.7° C. for the acetone containing system and at a minimum boiling azeotrope $x_{chloroform} = 0.47$ and 55.5° C. for the chloroform containing system. The van Laar form of equation was fitted to the activity coefficient—composition data to obtain the van Laar constants which best described the experimental data. These are: $A_{Chloro\text{-}DMB} = 0.188$, $B_{Chloro\text{-}DMB} = 0.265$; $A_{Acet\text{-}DMB} = 0.722$, and $B_{Acet\text{-}DMB} = 0.620$.

A MORE complete experimental knowledge of the characteristics of various types of vapor-liquid systems needs to be developed to aid in understanding and relating thermodynamic properties of mixtures. One of the many areas to be investigated is the behavior of multicomponent systems comprised of binary systems which show azeotropic characteristics—maximum, minimum, or both types. The two binary systems studied here were selected because both acetone and chloroform form minimum boiling azeotropes with dimethylbutane and form a maximum boiling azeotrope with each other. This forms an interesting ternary mixture which is under study.

EXPERIMENTAL

Materials. The 2,3-dimethylbutane as received had a guaranteed purity of 99 mole %, and the acetone and chloroform samples were reagent grade. No further purification was considered necessary. The properties of the materials are shown in Table I.

Procedure and Analysis. Vapor-liquid equilibrium data were determined in a modified Colburn still (*6*) described by Hollenshead and Van Winkle (*4*) and others (*3, 7*) using the same procedure. In brief, the procedure consists of making up the samples by weighing each component to obtain the range of desired charge compositions, transferring the cold prepared sample to the still, and boiling the sample at the correct recirculation rate. Adjustments in pressure are made to attain and maintain the pressure at 760 mm. of mercury (in this case) by pressuring the system through a regulator and surge tank with nitrogen. After steady state conditions are reached (based on constancy of temperature, pressure, and boiling rate) the still is operated for approximately one hour before shutting down, isolating the vapor and liquid samples, withdrawing them, and cooling them in ice water.

The samples in this investigation were analyzed with a Bausch and Lomb precision refractometer using previously laboratory-determined refractive index–composition curves. Temperatures were measured with a copper-constantan thermocouple in a glass sheath in contact with the boiling liquid surface and using a Type K precision potentiometer. Pressures were measured by means of a mercury-in-glass manometer, and the level was read by means of a precision cathetometer.

The established limits of error in the determination of the equilibrium data and measurement of the conditions are as follows:

Temperature	± 0.1° C.
Pressure	± 0.2 mm. of mercury
Composition	± 0.005 mole fraction

RESULTS

The vapor-liquid equilibrium data including temperature and mole fraction in the liquid and vapor are shown in

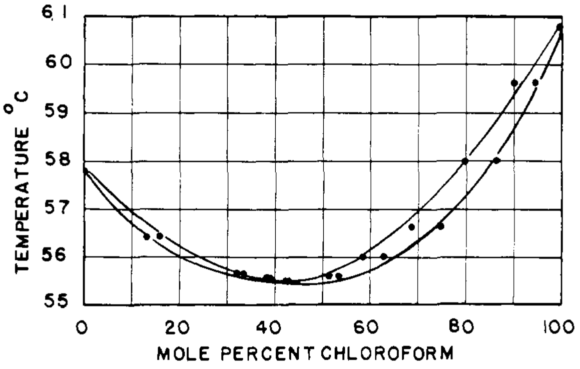

Figure 1. *t-x-y* data for chloroform-DMB

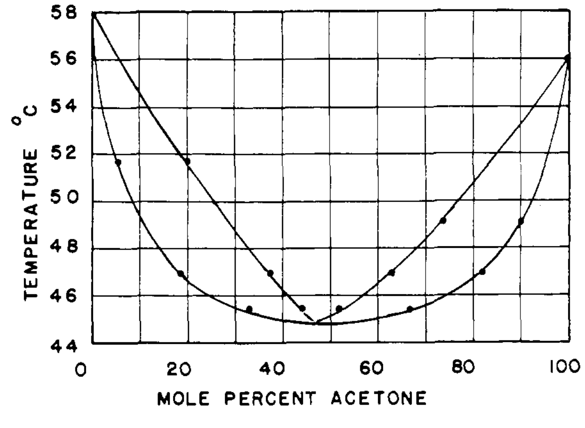

Figure 2. *t-x-y* data for acetone-DMB

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Table I. Physical Properties of Materials

	2,3-Dimethylbutane	Chloroform	Acetone
Boiling point °C. at 760 mm. Hg			
Experimental	57.80	60.8	56.0
Literature (2)	57.98	60.3	56.1
Refractive index, n_D^{25}			
Experimental	1.37232	1.44243	1.35633
Literature (2)	1.37231	1.44293	1.35662
Antoine constants (2)			
A	6.80983	6.90328	7.19038
B	1127.187	1163.0	1233.4
C	228.90	227.0	230.0

Table II. Binary System Vapor-Liquid Equilibrium Data

System: Chloroform (1), Dimethylbutane (2)[a]

t, °C.	x_1	y_1	γ, exptl.	γ_2, exptl.	γ_1, calcd.	γ_2, calcd.
60.8	1.00	1.00	1.00	...	1.00	1.84
59.6	0.945	0.902	1.03	1.69	1.00(3)	1.68
58.0	0.866	0.800	1.05(5)	1.49	1.01	1.51
56.6	0.750	0.687	1.09(5)	1.31	1.04(5)	1.33
56.0	0.626	0.585	1.14	1.18	1.09(5)	1.20
55.6	0.537	0.513	1.18	1.14	1.14	1.13
55.5	0.430	0.424	1.23(5)	1.09	1.20	1.08
55.6	0.387	0.390	1.24	1.07	1.23	1.06
55.65	0.325	0.336	1.27	1.05	1.27	1.04
56.4	0.132	0.155	1.42	1.02	1.42	1.01
57.8	0.00	0.00	...	1.00	1.54	1.00

System: Acetone (3), Dimethylbutane (2)[b]

t, °C.	x_3	y_3	γ_3, exptl.	γ_2, exptl.	γ_3, calcd.	γ_2, calcd.
56.0	1.00	1.00	1.00	...	1.00	4.17
49.1	0.900	0.739	1.05	3.40	1.01	3.27
46.9	0.820	0.630	1.07	2.95	1.04	2.75
45.4	0.668	0.520	1.15	2.19	1.16	2.02
44.8	0.465	0.485	1.57	1.49	1.51	1.44
45.4	0.331	0.442	1.96	1.26	1.95	1.21
46.9	0.186	0.373	2.80	1.11	2.82	1.07
51.7	0.060	0.201	3.92	1.04	4.22	1.01
57.8	0.00	0.00	...	1.00	5.27	1.00

[a] van Laar constants: $A = 0.188$, $B = 0.265$. [b] van Laar constants: $A = 0.722$, $B = 0.620$.

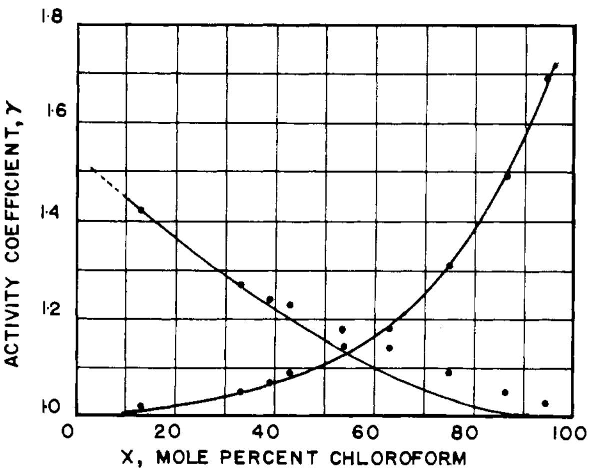

Figure 3. γ-x data for chloroform-DMB

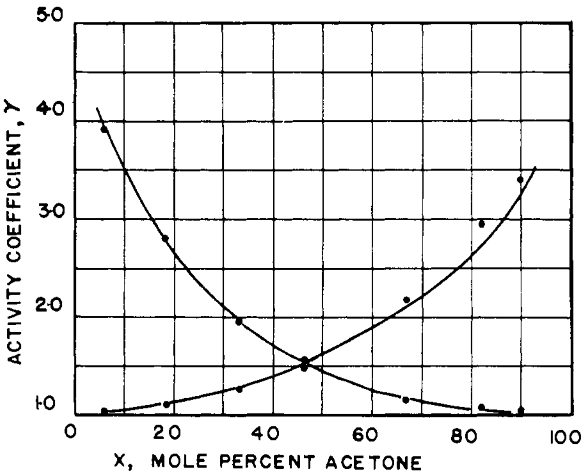

Figure 4. γ-x data for acetone-DMB

Table II. Included also are the experimental and calculated liquid phase activity coefficients and the Carlson and Colburn modified (*1*) van Laar constants. The *t-x-y* data are shown on Figures 1 and 2 and the γ-x data on Figures 3 and 4. The activity coefficients were calculated by

$$\gamma = \frac{yP_T}{xP}$$

where y, x = vapor and liquid equilibrium compositions, P = pure component vapor pressure, and P_T = total pressure. The authors assumed that at the pressure of the investigation, the deviation of the vapor phase from ideal behavior was small enough to be neglected. Similarly, the correction for the specific volume of the liquid was neglected for the same reason.

From a larger scale temperature-composition plot using the calculated data from the van Laar constants, $A_{\text{C-DMB}} = 0.188$, $B_{\text{C-DMB}} = 0.265$, $A_{\text{A-DMB}} = 0.722$, $B_{\text{A-DMB}} = 0.620$, the azeotrope compositions and temperatures were: acetone–2,3-dimethylbutane, $x_{\text{acetone}} = 0.47$, $t = 44.7°$ C.; chloroform–2,3-dimethylbutane, $x_{\text{chloroform}} = 0.47$, $t = 55.5°$ C. These compare, respectively, with the values reported in Horsley (*5*): $x_{\text{acetone}} = 0.42$, $t = 46.5°$ C.; $x_{\text{chloroform}} = 0.47$, $t = 55.5°$ C.

The van Laar constants were determined by an iterative method devised to reduce the deviation of all experimental data points from the van Laar-type curve. The values of the constants were adjusted until a minimum deviation from the activity coefficient composition curve was experienced.

The data were checked for consistency by the Redlich-Kister (*8*) method wherein the values of log γ_1/γ_2 were plotted *vs.* the mole fraction of the lighter component, and the areas between the curve above and below the zero log activity coefficient ratio were compared. (The Redlich-Kister method for consistency is based on Scatchard's excess free energy relation and assumes the vapor phase to behave ideally.) The curve represented the best fit of the data determined by a least squares method. The areas differed by 7.9% for the acetone-DMB binary and 10.6% for the chloroform-DMB system.

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Composition of the Branched Paraffin-Cycloparaffin Portion of Petroleum, 140° to 180° C.

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Thirty-eight hydrocarbons were isolated from the paraffin-cycloparaffin portion of petroleum boiling between 140° and 180° C. These are comprised of 13 branched paraffins, 17 monocycloparaffins, and eight bicycloparaffins. Together with 10 compounds isolated in previous investigations this accounts for 84% of the portion, or 10.2% of the total crude. The compounds were isolated by distillation and gas-liquid chromatography and identified principally by infrared, nuclear magnetic resonance, and mass spectrometry. Several of the compounds isolated—2,6-dimethyloctane, 2-methyl-3-ethylheptane, and 4-isopropylheptane—appear to be derived from the terpenoids and are of interest in connection with the genesis of petroleum.

THIS INVESTIGATION is part of the program of the American Petroleum Institute Research Project 6 on the composition of its reference petroleum (*15*). Specifically, it describes the analysis of the branched paraffin-cycloparaffin portion boiling from 140° to 180° C. The work was undertaken primarily to obtain information concerning the structures of the bicycloparaffin components.

The polycycloparaffins constitute an important class of petroleum hydrocarbons. In the higher molecular weight range, above C_{25}, they are more abundant than any other class, constituting, in many cases, from 30 to 50% of the material. Yet, relatively little is known concerning their molecular structures. The most favorable place to obtain structural information is with the bicycloparaffins in the lower molecular weight range, where it is still possible, because of the limited number of isomers, to separate individual compounds and in some cases establish their identity.

Of course, the branched paraffins and monocycloparaffins are also of interest and where possible they were separated and identified. Three of the branched paraffins isolated appear to be derived from the monoterpenoids.

PROCEDURE

The starting material consisted of all the paraffin-cycloparaffin portion boiling from 140° to 180° C. except for samples of 10 hydrocarbons isolated in previous work. These hydrocarbons and their normal boiling points are